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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : G01N 30/06, 30/30 — A1

(11) International Publication Number: **WO 98/21574**

(43) International Publication Date: 22 May 1998 (22.05.98)

(21) International Application Number: PCT/AU97/00764

(22) International Filing Date: 11 November 1997 (11.11.97)

(30) Priority Data:
PO 3559 11 November 1996 (11.11.96) AU

(71) Applicant *(for all designated States except US)*: ROYAL MELBOURNE INSTITUTE OF TECHNOLOGY [AU/AU]; 124 Latrobe Street, Melbourne, VIC 3000 (AU).

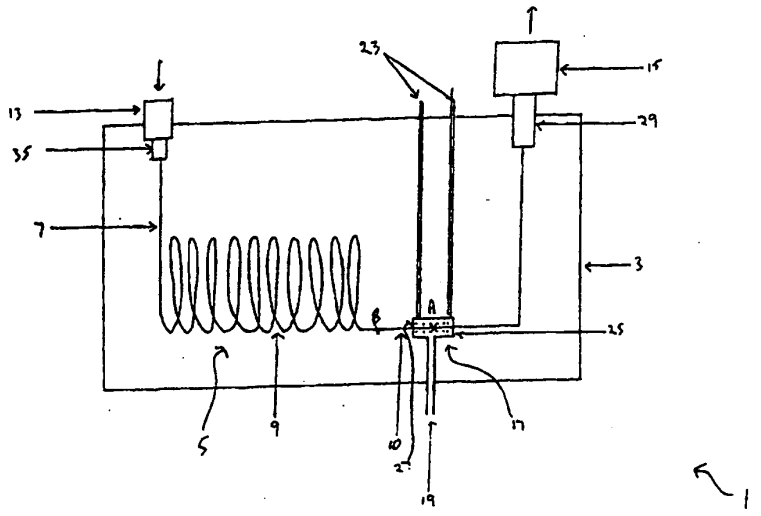
(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: MARRIOT, Philip [AU/AU]; RMIT– Department of Applied Chemistry, 124 La trobe Street, Melbourne, VIC 3000 (AU).

(74) Agent: ROLLS, Carolyn, Lesley; Griffith Hack, 509 St. Kilda Road, Melbourne, VIC 3004 (AU).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
With amended claims and statement.

(54) Title: APPARATUS AND/OR DEVICE FOR CONCENTRATION



(57) Abstract

An apparatus and/or device for the concentration of chemical components of a chemical sample comprising a conduit means and a cooling means, said conduit means having a receiving port for receiving the chemical sample and an outlet port for expelling the chemical sample, said ports being in fluid communication with each other, said cooling means capable of cooling a portion of the conduit means and the chemical sample therein, said cooling means moveable relative to said conduit means such that at any one instant a portion of the conduit means and the chemical sample therein is cooled by the cooling means so that movement of the chemical sample therein is at least decreased.

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APPARATUS AND/OR DEVICE FOR CONCENTRATION

The present invention relates generally to the field of chemistry, and in particular to chemical analysis techniques. More particularly, the present invention relates to an apparatus and/or device for the concentration of chemicals of a chemical sample. A particular chemical analysis technique is chromatography, in all its general and specific forms. In particular, the present invention relates to an apparatus and/or device for the concentration of chemicals of a chemical sample in the gas, mobile or carrier phase using thermal modulation to alter the rate of flow of the chemicals along a column of a chromatograph, particularly a gas liquid chromatograph. The invention particularly relates to an apparatus for the concentration of chemicals using a moveable heat modulator to concentrate a band of a chemical, particularly along the column of a chromatograph. It is to be noted that heat modulation includes both heating and cooling of the sample.

Gas chromatography is one analytical technique used to separate different chemicals within a single chemical sample. Using this method, as a chemical sample flows along a column each chemical present in the sample is separated into a band. Each separated band of chemical may be detected as a peak by a detector. Ideally each of the chemicals is separated into a discrete band. However, in reality, often the bands are far from discrete, the bands being either broad and/or overlapping with each other. For ease of interpreting results of a gas liquid chromatograph and to assist in accurately identifying, in particular, chemical compounds in a sample being analysed it is desirable to have chromatographic peaks of a somewhat acicular shape, and being separated from each other with little or no overlapping.

In an attempt to obtain discrete bands one or more of the separated bands of chemicals may be passed through a second column where further chromatographic separation occurs. In some instances only a portion of the band is passed into the second column for further separation. However, the bands, without cooling, often broaden as they pass through the second column.

Many methods in gas chromatography involve some degree of retardation or alteration of the velocity of the chromatographic band; the variety of techniques used to achieve this include those based upon by supplementary cooling, heating or phase ratio adjustment.

An example of the former is cryogenic trapping of solute in methods such as purge and trap (as described in Jursik, T., Stransky, K. and Ubik, K., J. Chromatogr., 586 (1991) 315; Kalman, D., Dills, R., Perera, C. and DeWalle, F., Analyt. Chem., 52 (1980) 1993; Hagman, A. and Jacobsson, S., J. Chromatogr., 448 (1988) 117) and more recently the Varian Fast GC method (as described in Varian Chromatography Systems, GC Advantage Note 9), along with cooling of heart-cut fractions in multidimensional gas chromatography (as described in Schomburg, G., J. Chromatogr., A703 (1995) 309). Elevated temperature has been used by Phillips in his novel metal-film coated capillary column method (described in Phillips, J. B., Luu, D., Pawliszyn, J. B. and Carle, G. C., Analyt. Chem., 57 (1985) 2779; Liu, Z. and Phillips, J. B., J. Microcol. Sep., 2 (1990) 33). In this method electrical heating of the coated column allowed rapid movement of the solutes through this heated section and led to such advantages as detection modulation (as described in Liu, Z. and Phillips, J. B., J. Microcol. Sep., 6 (1994) 229) and the recently described whole-column variable temperature gradient methods (described in Phillips, J. B. and Jain, V., J. Chromatogr. Sci., 33 (1995) 541; Jain, V. and Phillips, J. B., J. Chromatogr.

Sci., 33 (1995) 601. Phillips has described a rotating heater which is able to speed up and accumulate a sample which enters the region affected by the heater.

Phase ratio adjustment is usually used to provide a measure of trapping of solute in procedures such as those which use retention gaps (as described in Jennings, W., Analytical Gas Chromatography, Academic, Orlando, 1987) and the Grob solvent effect (an approach using temporary pseudo phase-ratio decrease during injection, which has been described in Grob, K., Split and Splitless Injection in Capillary GC, 3rd ed., Huthig Buch Verlag, Heidelberg, 1993). Such a feature has been recently used in conjunction with large volume sample injection (as described in Vreuls, J. J., Moy, H. G. J., Jagesar, J., Swen, R., Hessels, R. E. and Brinkman, U. A. Th., Proceedings of the Sixteenth International Symposium on Capillary Chromatography, Riva del Garda, Italy, 27-30 September 1994, pp 1181).

However, in the techniques described above, the analyte trapping step needs to be followed by analyte re-mobilisation, and this presents a considerable challenge in some designs. With "solvent effect" trapping where the oven is set below the boiling point of the injection solvent, remobilisation occurs by allowing the solvent to evaporate, leaving the focussed solutes to begin migrating when the oven temperature increases. Other methods relying on construction of cooling and heating devices may require more ingenuity to obtain the desired effect. Thus cryogenic traps which use liquid CO_2 or N_2 coolant have been described for the focussing step, but the remobilisation imposes strict requirements on trap construction in order to retain the narrow solute distribution which has been achieved in the trapping step. In "FASTGC", solute is trapped in a cooled metal tube which can then be rapidly capacitively heated at a reported 100,000°C/sec to backflush solutes into the chromatographic

column. This has been described for example in Ewels, B. A. and Sacks, R. D., Analyt. Chem., 57 (1985) 2774; Mouradian, R. F., Levine, S. P. and Sacks, R. D., J. Chromatogr. Sci., 28 (1990) 643; Lanning, L. A., Sacks, R. D., Mouradian, R. F., Levine, L. A. and Foulks, J. A., Analyt. Chem., 60 (1988) 1994; Rankin, C. L. and Sacks, R. D., J. Chromatogr. Sci., 32 (1994) 7. Injection peak widths of the order of milliseconds have been quoted in Lanning *(ibid)*. This is significantly smaller than that arising from routine GC injection. It is also known to simply allow a cryo trap to warm to oven temperature by turning off the cryo fluid. This gives narrowed peaks, but is not a particularly elegant method. This procedure is used in some multidimensional cryogenic traps (such as those described in Cortes, H. J., ed. Multidimensional Chromatography, Techniques and Applications. Chromatographic Science Series, Vol. 50 (1990)), where the heart-cut fractions are directed to a trap at the start of the second column. By cooling the oven, switching off the coolant to the trap and then going through a second temperature program analysis, the second column chromatographic elution is performed. Generally the trap focussing is quite effective. Yet other approach use supplementary heating in the same region as the cryo cooling, to rapidly heat the column zone which contains the trapped analyte. Typically, the heater is some type of wire-wound heater or tubular metal which can be rapidly heated by electrical means. This can be done with the cryogenic coolant still on, so the cool/heat cycle is controlled just by the electrical heating event. In such a design the requirement to have cooling and heating in the one device presents a conflict in the demands placed on device construction, and so is difficult to control as desired when a capillary column is placed in the device.

Heat modulation techniques do produce sharper, more discrete bands. However, heat modulation techniques

require large and fast changes in temperature to be effective. If the temperature drop or rise is too slow, broad indiscrete bands of two or more chemicals are likely to result thus leading to interpretational difficulties. If the temperature change is not large enough the chemical sample will not be immobilised sufficiently and broad indiscrete bands are likely to result.

Large changes in temperature over a short period in time are energy demanding. The temperature of the column at any one section may change in temperature from below 0°C to 200-300°C in one second. Hence techniques using temperature modulation are energy demanding and thus expensive and rapid heat/cool/heat cycles are not practical. As a result of the significant temperature changes necessary for heat modulation, heat modulation techniques tend to have only one heating event.
It is an aim of the present invention to provide an apparatus or device able to produce discrete bands of chemicals from a chemical sample and to provide a method of producing discrete bands of chemicals from a chemical sample which is more energy and time efficient and which results in more discrete bands of chemicals with a minimum of overlap.

The present invention provides an apparatus and/or device for the concentration of chemical components of a chemical sample comprising a conduit means and a cooling means, said conduit means having a receiving port for receiving the chemical sample and an outlet port for expelling the chemical sample, said ports being in fluid communication with each other, said cooling means capable of cooling a portion of the conduit means and the chemical sample therein, said cooling means moveable relative to said conduit means such that at any one instant a portion of the conduit means and the chemical sample therein is cooled by the cooling means so that movement of the chemical sample

therein is at least decreased.

The apparatus and/or device may be incorporated into or associated with a chromatographic column, or any spectroscopic, separation or detection apparatus. A chromatographic column may be part of any type of chromatograph such as, for example, a supercritical fluid chromatograph, a gas liquid chromatograph, a gas solid chromatograph, a micro column liquid chromatograph or a high performance liquid chromatograph. Preferably the apparatus or device is incorporated into a chromatographic column such that the conduit means forms part or all of the column. Preferably the chromatographic column has two or more sections. The conduit means may form part or all of each or both sections of the chromatographic column or the conduit means may bridge the two sections. Each section of the chromatographic column may be of the same or of different diameter. The sections of the chromatographic column may be formed independently or integrally.

The conduit means maybe a tube , such as a circular, square or rectangular tube. The tube may be formed in any shape including linear, looped, wound or bent. The tube may be wrapped around a support member or bent over a planer surface.

The conduit may be of any length and dimensions. Where the conduit contains more than one section, each section may be of the same or different lengths. The conduit may be part of a column such as for example a liquid chromatography column, a capillary liquid chromatography column, a packed gas chromatography column, a capillary gas chromatography column or a supercritical fluid column. A liquid chromatography column may be from 5 cm to 50 cm long with packing material inside; a capillary liquid chromatography column may be from 1 metre to 10 metres long with a narrow internal diameter, with or without internal packing; a

packed gas chromatography column may be between 0.5 metres and 5 metres long; a capillary gas chromatography column may be from 5 metres to 50 metres long.

Preferably the conduit is made of stainless steel, glass, fused silica, or other metal or glass-lined metal.

Preferably the conduit contains a carrier fluid to carry the chemical sample which is to be concentrated from the receiving port to the outlet port. The carrier fluid may be a gas, liquid or supercritical fluid. The type of carrier fluid in the tube may depend on the type of chemicals present in the chemical sample. Where the conduit comprises more than one section, the carrier gas in each section may be of different composition and/or velocity.

The conduit may also contain a stationary phase. Where the conduit comprises two or more sections, the stationary phase in each section may be of the same or varied thicknesses. The stationary phase in each section may be of the same or different compositions. Some sections of the conduit may have no coating or stationary phase.

In one embodiment the conduit comprises three sections, a first separating section, a concentrating section and a second separating section. The first separating section is contained within a housing which has a variable temperature of between ambient and 300°C. The second separating section is contained within a housing which also has a variable temperature of between ambient and 300°C. The cooling means is located on the concentrating section of the conduit. All or part of the chemical sample may pass through the second separating section.

The chemical sample may comprise one or more different types of chemicals or components. The apparatus may

concentrate one type of chemical at a time from the chemical sample or it may concentrate several types of chemicals together.

The chemical sample to be concentrated may be in a solid, liquid or gas phase. Preferably the chemical sample is in a liquid phase and the chemical sample is injected into the receiving port. The introduced sample may be derived from a thermal desorption device or from a head-space gas sampler, whereby volatile compounds enter the conduit over an extended period of time.

The chemical sample to be concentrated may contain any chemical components, including volatile organic and inorganic compounds, pesticides, chemical pollutants, semi-volatile compounds, petroleum products, synthetic organic compounds, drugs and other such compounds which may be suitable for chromatography separation and analysis.

The chemical sample may be a sample of a chemical cocktail, a body fluid such as blood urine, faeces or the like, soil samples, water, products of chemical reactions, or a liquid, solid or gas extract fraction of another sample.

Preferably the apparatus or device comprises a means for converting the chemical sample into a gas phase if the chemical sample is not already a gas. Preferably the chemical sample is vaporised after entering the receiving port and before flowing through the conduit.

Preferably a detector means is connected to the outlet port. The detector means is a means of converting some chemical or physical property of the chemical compound into a measurable electronic response. The detector means is able to detect the chemicals present in the chemical sample. The detector means may be of any type appropriate to detect chemicals in the chemical sample or chemicals

suspected of being in the chemical sample. Typical examples of detector means which may be used in the present invention include mass spectrometry, any of the ionisation-type detectors, spectroscopic detectors and the like. Preferably a display means is connected to the detector means. The display means is able to indicate the presence of certain chemicals in the chemical sample. Typical examples of display means which may be used in the present invention include chart recorders, electronic data collection means, electronic integrators or computer acquisition and display.

The cooling means may be any standard known cooling means. The cooling means may comprise refrigerants such as for example carbon dioxide and liquid nitrogen. The cooling means may be an electrical cooling (thermoelectrical cooling) system such as a peltier cooling device, where the cooled side of the device is used to cool the separation means. Preferably the cooling means is between 0.1 mm and 500 mm in length. More preferably the cooling means is between 5 mm and 50 mm in length.

The cooling means may be moved relative to the conduit means manually or automatically. The cooling means may be moved relative to the conduit means manually by an operator. The cooling means may be moved automatically by hydraulic means, magnetic means, mechanical means or electronic means. Movement may be automatic, pre-programmed, computer controlled or the like.

Preferably the movement of the cooling means is pre-programmed so that the cooling means moves automatically at a predetermined time, or time rate of change.

The cooling means may be moveable in relation to the conduit so as to be capable of cooling any portion of the conduit. The cooling means may be moved relative to the

conduit in the direction of the flow of the chemical sample or against the direction of flow of the chemical sample. Movement may be continuous or may be interrupted or sequential.

Preferably the cooling means is such that the motion of the cooled chemicals is reduced by at least 10 fold compared to the chemicals in the portion of the conduit which are not cooled. Preferably the chemicals in the cooled section are cooled to an extent that they are basically motionless.

Preferably the cooling means can cool the chemical sample to a temperature between -20°C and 100°C. Preferably the cooling means cools the chemical sample to a temperature of between 100°C and 150°C less than the chemical sample in the remainder of the conduit.

In one embodiment the portion of the conduit not subjected to the cooling means is subjected to a heating means. The heating means may be any standard heating means such as a wire wound heating tape or tube. The temperature of the heating means may be variable. The heating means may be fixed or moveable. The portion of the conduit not subjected to the cooling means may be subjected to the temperature of the ambient surrounds of the conduit.

The cooling means may be fixed and the conduit may be moveable. The tube may be fixed and the cooling means may be moveable. Preferably the conduit is threaded through the cooling means, the conduit being fixed and the cooling means is slidable along the outside of the conduit.

In a preferred embodiment, the conduit is fixed. The cooling means comprises a sleeve between 10 mm and 100 mm in length. The sleeve is fitted over the conduit and slidable along the tube. The sleeve is hollow and has one or more entry ports in fluid communication with the hollow

and one or more exit ports in fluid communication with the hollow. Cool coolant gas flows through the entry ports into the hollow and out the exit ports. The cool coolant fluid is warmed by the conduit and the chemical sample in the region of the conduit around which the sleeve is fitted while flowing from the entry ports to the exit ports and expands, hence the flow of coolant fluid cools the tube and the chemical sample in the region of the conduit around which the sleeve is fitted. In a preferred embodiment the conduit is located within a housing containing a heating means and coolant gas passes from the cooling means into the housing. The cooling means may remain in one position relative to the conduit for any length of time. The cooling means may be moved relative to the conduit depending upon the chemicals being concentrated. Where the conduit also contains a carrier gas and/or a stationary phase, the carrier gas and/or the stationary phase may also affect the frequency at which the cooling means is moved in relation to the conduit.

The cooling means may also comprise a slotted tube or similar arrangement, with part of the conduit, such as concentrating section, brought into the cooling means by insertion into the cooled slot. The conduit can be brought up into the slotted tube, to allow cooling, and then brought away from the cooling means to allow remobilisation. The cooling means can be moved onto or away from the conduit. This type of operation can be done with an electrically cooled device also.

The cooling means may be held stationary relative to the conduit for any period of time. A sample may be concentrated for a period of one to two minutes by maintaining the cooling means in a stationary position for one to two minutes. Where a conduit comprises two or more sections and all of the components are to be passed to the second section of the conduit by the heart-cut method, the

cooling means may be held stationary relative to the conduit for up to 30 minutes or longer. If a sample is to be modulated into a detector the cooling means may be moved as rapidly as 5 or more times per second. One or more components of the sample may be concentrated by the cooling means.

Preferably the cooling means moves relative to the conduit at a speed of between 1 cm per second and 20 cm per second, preferably between 1 cm per second and 20 cms per second, the rate depending on the dimension of the conduit and the mode of movement of the cooling means.

The cooling means may be positioned anywhere along the conduit. The cooling means may be positioned immediately after the receiving port in the entry section or immediately prior to the outlet port in the expulsion section or elsewhere along the conduit. Where the conduit consists of more than one section the cooling means may be positioned on any one of the sections. The cooling means may be moveable between each section of the conduit. Preferably the cooling means is located in an area midway along the tube.

Preferably, where the sample is introduced by thermal desorption or is introduced into the receiving port over an extended period of time, such as with a gas process stream, a cooling means is located prior to a separation section of the conduit so that the sample is concentrated before being separated to obtain faster and more discrete separation. The chemical sample may pass through a second cooling means after it has been separated.

The temperature of the cooling means may be fixed or adjustable.

In one embodiment, the apparatus comprises two or more

cooling means moveable relative to the conduit. A cooling means may be located at either end of a separation section of the conduit. In one embodiment the apparatus comprises a conduit having two separation sections and two cooling means moveable relative to the conduit, one cooling means located at the end of the first separation section and the second cooling means located at the end of the second separation section prior to a detection means.

In a preferred embodiment the apparatus comprises a conduit consisting of three sections, a first section, a connecting section and a second section. The connecting section is linear. The cooling means is moveable along the connecting section. The chemical sample is injected into a receiving port and vaporised before flowing along the first section. In the first section the chemicals in the chemical sample are roughly concentrated or separated into chemical bands. The chemical sample then flows through the connecting section until it reaches an area of the conduit subjected to the cooling means. The first chemical band reaches the area of the conduit subjected to the cooling means first. Depending on the temperature of the cooling means the chemical sample subjected to the cooling means is either slowed or stopped in the cooled section, hence concentrating the chemical bands in the cooled section. Once all of a chemical band from the chemical sample has been stopped or slowed by the cooling means the cooling means is then moved along the connecting section to another area. On movement of the cooling means along the conduit, the chemical band which has been slowed or frozen is remobilised by ambient heat or a heating means and begins movement along the second section. Upon reaching the end of the second section, the concentrated chemical band is expelled from the outlet port in a sharp band which is detected by a detector means and relayed to a display unit.

In a preferred embodiment the apparatus comprises a

branched conduit. The chemical sample enters a first section of the conduit and travels along the conduit until it reaches a branch in the conduit. A first portion of the chemical sample travels along a first branch to a first detection means. A second portion of the chemical sample travels along a second branch until it reaches a second detection means. A conduit may have one or more branches. Preferably when the conduit is branched, the cooling means is positioned in an area before the branch such that the cooling means is capable of cooling all of the chemical sample. The first and second portions may be of the same or different sizes. Each portion may be selected from any part or parts of the chemical sample. In another embodiment, a cooling means may be located in one or more of the branches to concentrate chemical bands directed to the branch from the first section of the conduit.

In another aspect of the invention there is provided a method of concentrating chemicals in a chemical sample comprising the steps of a) inserting the chemical sample into a conduit and allowing the chemical sample to travel through the conduit; b) cooling a first portion of the conduit to a predetermined temperature and maintaining the predetermined temperature using the cooling means; c) accumulating within the first portion of the conduit for a predetermined period of time a portion of the chemical sample, thus forming a first concentrated band; d) moving the cooling means to a second portion of the conduit and allowing the first portion of the conduit to warm so as to release the first concentrated band of the chemical sample within the first portion of the conduit; and e) repeating steps c) to d) as many times as desired.

Preferably the method of concentrating chemicals in a chemical sample comprises the steps of a) inserting the chemical sample into a conduit containing a carrier fluid to carry the chemical sample through the conduit; b)

cooling a first portion of the conduit to a predetermined temperature and maintaining the predetermined temperature with a cooling means ; c) accumulating within the first portion of the conduit for a period of time the chemical sample carried thereinto by the carrier fluid, thus forming a first concentrated band; d) moving the cooling means to a second portion of the conduit and allowing the first portion of the conduit to warm so as to release the first concentrated band of the chemical sample within the first portion of the conduit and e) repeating steps c) to d) as many times as desired.

The use of a cooling means to collect of "trap" fractions of the chemical sample can offer advantages in the multidimensional gas chromatography (MDGC) analysis system. In one variant of the technique, once the first dimension is eluted the oven is cooled, the cooled section of the conduit is allowed to return (warm) to oven temperature, then the oven temperature programmed to enable the heart-cut fractions to be chromatographed. The use of non-cryogenic MDGC with direct analysis on a second column has been reported in Kinghorn, R. M. and Marriott, P. J., Proceedings of the Eighteenth International Symposium on Capillary Chromatography, Riva del Garda, Italy, 20-24 May, 1996. It has been noted however that the lack of focussing can lead to poorer results in some instances. The present invention can be used to permit each heart-cut fraction to be effectively focussed, and efficiently remobilised at the operating oven temperature, and so maintain the high resolution of the system.

The invention will now be described with reference to the following Figures and examples.

- Figure 1 is a partial schematic side elevation view of an apparatus for the concentration of chemicals of a chemical sample according to the present invention comprising one separating column.

- Figure 2 is a partial schematic side elevation view of an apparatus for the concentration of components of a chemical sample according to the present invention comprising two separating columns.
- Figure 3 is a partial schematic side elevation view of an apparatus with a concentration of components of a chemical sample according to the present invention having a cooling means located prior to a separation means.
- Figure 4 is a schematic design of longitudinally modulated cryogenic system:

(a) illustrates one of the possible mechanisms for movement of the cooling means, with the cooling means moved from position A to position B to allow the trapped fraction to then be heated by the oven and continue its travel to the detector;

(b) presents a sketch of the arrangement of the assembly in the GC oven, with a manual or other control providing the means of relative movement of the column and cooling means. The arrow at A indicates the longitudinal modulation movement of the arm which causes the capillary column to move through the cooling means.

- Figure 5 depicts two typical modulation processes representing the cooling means and remobilisation of solute:

(a) illustrates the chromatographic peak positions in a simulated chromatogram;

(b) describes an extended period of the trap in the trapping (collection) position to quantitatively trap each individual solute, followed by a rapid release step immediately following each trapping period;

(c) shows that the trap cryogenic fluid is not turned on until after the fourth peak has eluted, then the subsequent peaks 5 to 7 are trapped and eluted as one group after the final peak has been trapped.

- Figure 6 depicts gas chromatographic traces of a hydrocarbon mixture of octane through tridecane by using three different operations of the cooling means.

Chromatography conditions: 110°C isothermal, carrier (He) gas at 19.8 cm/s for 6(a) and 6(b), and 16.7 cm/s for 6(c)-(e). Response scales are the same for (a) and (b).

(a) The cryogenic fluid for the cooling means was turned off, so this is a regular isothermal GC trace.

(b) The cooling means was cooled with CO_2 for the whole analysis and was moved approximately 15 seconds after each peak had been fully collected, as described in the Figure 5(b) process.

(c) The cryogenic fluid for the cooling means was turned off, so this is a repeat regular isothermal GC trace.

(d) The coolant for the cooling means was not introduced until after C_{11} had passed. Thus C_{12} and C_{13} were trapped together, then eluted when the cooling means was moved after the C_{13} elution. Peaks C_8 to C_{11} are the same as their respective peaks in 6(c). This process is described by Figure 5(c).

(e) An expanded view of the C_{12} and C_{13} solute separation shown in Figure 6(d).

Figure 7 depicts gas chromatograms of C_{14} methyl ester. The conditions used were the same as the conditions used for Figure 6 except isothermal oven temperature of 200°C. Note that different response scales are used, with (a) having a more sensitive response setting.

(a) The cryogenic fluid for the cooling means was not turned on, so this is the regular GC trace.

(b) The cooling means was turned on at approximately 6 min to allow the ester to be trapped. The cooling means was moved at 10.0 min to remobilise the solute, and the ester was detected 16 seconds later.

(c) The solute was trapped, then the cooling means was moved in 1 cm steps away from the detector, commencing at 10.0 min. The ester was eluted with a retention of 14.12 min, thus indicating that the cooling means had to almost be fully removed from the cooling region - that is, to point B in Figure 4(a) - before the

solute was remobilised. Hence the solute was effectively trapped in the first 1 cm of the cooled column region.

In Figure 1 there is shown a gas liquid chromatograph 1, hereinafter referred to as a GLC. The GLC comprises a housing 3. The inside of the housing 3 is maintained at a constant or variable temperature of between 60°C and 300°C by a heating means. The heating means, which is not shown, is an electric element. A tube in the form of a column 5 is contained within the housing 3. The column 5 comprises three sections, an entry section 7, a helical separation section 9 and a concentration section 10. The entry section 7 is approximately 10 centimetres long. The separation section 9 is a capillary gas chromatograph column approximately 25 metres long. The concentration section 10 is approximately 1 metre in length. The separation section 9 is in fluid communication with, at one end, the entry section 7 and, at the other end, the concentration section 10. The column 5 is made from glass and packed with a liquid coated inert solid support.

A vaporising port in the form of a vaporiser 35 is connected to the free end of the entry section 7. A receiving port in the form of an injection port 13 is connected to the free end of the vaporiser 35. The free end of the injection port 13 extends to the outer side of the housing 3.

An outlet port 29 is in fluid connection with the concentration section 10 of the column 5. The outlet port is in fluid connection with a chromatographic detector 15. The chromatographic detector 15 extends to the outer side of the housing 3.

A cooling means in the form of a cooler 17 is located on the concentration section 10 of the column 5. The cooler is maintained at a temperature of approximately 0°C. The cooler 17 is moveable relative to the concentration section

10. The cooler 17 has an entrance port 19 and two exit ports 23. The cooler 17 has a body 25 with a cavity 27. Part of the concentration section 10 is encased within the cavity 27 of the body 25. Each of the exit ports 23 and the entrance port 19 extend to the outer side of the housing 3. In use a cooling fluid such as carbon dioxide is introduced into the entrance port 19. The carbon dioxide flows through the body 25 of the cooler 17 around the cavity 27 cooling part of the concentration section 10 of the column 5 and any substance therein and flows out either exit port 23. The cooler 17 is moveable along the concentrating section 10 of the column 5 via electronic means which is not shown.

In use a chemical sample containing chemicals such as octane, nonane and decane is injected into the injection port 13 in a liquid phase. The sample is converted into a gas phase at the vaporiser 35. The sample flows through the entry section 7 the separation section 9 in which the chemical sample is separated and then into the concentration section 10. In the separation section 9 the chemical sample is separated into bands of discrete chemical components. The first chemical band exiting the separation column being the most volatile chemical, octane, followed sequentially by nonane and decane, chemicals which are less volatile or less easily eluted.

The cooler 17 which is located at point A cools the chemical components in the sample as they emerge from the separation section 9 and holds or reduces the mobility of the chemicals in the sample for a predetermined period of time. The first most volatile chemical, octane, is immobilised by the cooler 17. After a predetermined period sufficient to concentrate the whole of the band, approximately 5 to 20 seconds, the cooler 17 is moved along the concentration section 10 of the column 5 to point B. Point A and point B are approximately 2.5 cm apart. It

takes between 0.1 and 1 seconds to move the cooler 17 from point A to point B. Preferably the predetermined period is a period such that at least the first band of chemical, the most volatile, octane, separated from the chemical sample is immobilised to an extent that it has been concentrated in the concentration section 10 of the column 3 encased by the cooler 17. On moving the cooler 17 along the concentration section 10 the concentrated octane band is warmed by the electric element and hence is remobilised. The concentrated octane band then flows through the remainder of column 5 out the exit port 29 to the chromatographic detector 15. The chromatographic detector 15 then detects the octane which has been separated from the chemical sample as it is remobilised and passes through the chromatographic detector 15.

The second band of separated chemical, nonane, moving less rapidly than the first chemical along the separation section 9 is then immobilised by the cooler 17 at point B. The steps of immobilising and mobilising chemical bands or parts thereof from the chemical sample can be repeated as many times as desired. All of a chemical, part of a chemical or several chemicals may be concentrated together.

The apparatus shown in Figure 2 is the same as that shown in Figure 1 except that the apparatus in Figure 2 has a second separation tube. The numbers given to the components in Figure 1 correspond with the numbers given to the components in Figure 2.

In Figure 2 the concentration portion 10 of the tube 5 is located between the first separation section 9 and a second separation section 51.

The second separation section 51 is in fluid connection at one end with the concentration section 10 of the tube 5 and at the other end, in fluid connection with an expulsion

section 53 of the tube 5.

The outlet port 29 is in fluid connection with the expulsion section 53 of the column 5. The outlet port 29 is in fluid connection with a chromatographic detector 15. The chromatographic detector 15 extends to the outer side of the housing 3.

The apparatus shown in Figure 2 operates in a similar way to the apparatus shown in Figure 1. In the apparatus shown in Figure 2, once the chemical bands have been concentrated in the concentration section 10 of the tube 5 they are further separated in the second separating section 51 of the tube 5 before passing to the detector 15 via the expulsion section 53 of the tube 5.

The apparatus shown in Figure 3 is the same as that shown in Figure 1 except that in the apparatus shown in Figure 3 the cooler 17 is located in the entry section 7 of the column 5. The numbers given to the components in Figure 1 correspond with the numbers given to the components in Figure 3.

The apparatus shown in Figure 3 operates in a similar way to the apparatus shown in Figure 1. The chemical sample may be introduced into the injection port, either by injection or by extended sample introduction such as from a petroleum gas process stream, which is not shown, over a period of approximately 30 seconds. The chemical sample is concentrated in the entry section 7 before it is separated in the separation section 9 so as to produce more discrete bands when the chemicals are separated. The chemical sample once separated in the separation section 9 passes through the exit section 37 of the column 5 to the outlet port 29.

In Figure 4, the effluent from a first column passes into

the region which can be cooled to trap components of the chemical sample. With the cooling device positioned in its "trapping" position (*eg* Figure 4(a), position A) any components entering the cooling region are trapped, and focussed into a narrow band. By rapidly moving the cooling device to its remobilisation position (*eg* Figure 4(a), position B) the band is then moved into a second column. Ideally the second column should provide conditions suitable for rapid analysis, such as would arise from use of a short column of high phase ratio (thin film coating). When the cooling means is moved to position B, the previously collected band enters the second column region, where its combined components may be rapidly separated.

During this period, the cooling region will continue to collect effluent and any components from the first column will be effectively focussed as above. The cooling device is brought back to position A at an appropriate time, and after a suitable time period, the device is again rapidly moved to position B, thereby sending the next concentrated and focussed band to the second column.

This process can be repeated continually and at a repetition rate determined by the analysis requirements. Typically the first separation means and second separation means will possess different separation characteristics (such as different capacity factors for particular chemical species), and so can allow separation of components not separated in the first separation means.

One of the outcomes of this process is that a three-dimensional display of the chromatographic separation may be achieved, especially if the second separation occurs in a very short time frame, and thus the frequency of operation may be rapid in order to give a three-dimensional shape to the overall separation problem.

Example 1

A Shimadzu GC-17 (Shimadzu Oceania, Sydney, Australia) with flame ionisation detection and split/splitless injection was used in the Example. Split injection was used throughout. Helium carrier gas was employed. A BPX35 capillary column (available from SGE International, Ringwood, Australia) of dimensions 25 m x 0.2 mm inner diameter and film thickness 0.25 μm was used.

Figure 4(a) illustrates the position of the conduit means, the capillary column 1 with respect to the cooling means 3, inside a GC Oven, represented by the rectangle. In the assembly, the column 1 is moved longitudinally within the cooling means 3. The carrier within the capillary column moves in the direction of the arrow, while the trap moves in the opposite direction to elute solute. The carrier moves in a direction from an injector towards a detector.

With reference to Figure 4(b), the cooling means 3 was constructed from hypodermic stainless steel, with an outer tube of dimension 7 cm by 3.5 mm and a centre inner tube of 0.5 mm inner diameter which protruded 0.3 mm from the ends of the outer tube. The tubes were sealed at the end to create a cavity, with the inner tube left open to accommodate a capillary column. Cryogenic fluid (CO_2) enters through a 1/16" stainless steel inlet tube 5, and the vapour is vented through 1/8" tubing 7 outside the GC oven.

When in the solute collect position (that is, position A in Figure 4(a)), the cooling means was located about 25 cm from the detector end of the column, that is, the column length from trap to detector was 25 cm. Chemicals used were obtained from PolyScience Corporation (Niles, Illinois) standard mixture kits, and used as received. Standards were made up in analytical reagent grade hexane.

A component of the sample alkane was trapped in a subambient portion of the column, then the column was either moved towards the detector so as to bring the section of column with the focussed analyte band out of the cooled region, whereupon it heated up rapidly and the solute continued its travel to the detector, or the cooling means was moved away from the detector to reveal the original cooled region with trapped analyte, which then heated up and continued its migration.

The cooling means was operated so as to trap and release each individual solute, or to trap a number of solutes and then remobilise them as a packet of solutes, which then moved towards the detector and again separated into discrete peaks on the short length of capillary between trap and detector. An uncoated length of transfer column resulted in rapid travel time between trap and detector, and did not lead to component separation.

Figure 5 is a number of different modulation schemes which may be used for the above situation. In each of these, whole chromatographic bands are trapped. With rapid modulation, it is conceptually possible to "pulse" chromatographic peaks into a detector and thereby improve detection limits and sensitivity. The collect position refers to the cooling means in location A, Figure 4(a), whilst the release position is when the cooling means has been moved to location B, Figure 4(a), at which time the cooling means is moved clear of the condensed band, allowing the band to warm up and continue moving along the column.

A consequence of the trap and release as shown in Figure 5 is that the "broad" migrating chromatographic band is focussed and then released as a very narrow, concentrated peak. Its shape still approximates a symmetrical (gaussian) curve (at least when a length of coated

capillary is between cooling means and detector), but the resultant narrowness yields a dramatic increase in peak height.

The sample alkane mixture was chromatographed isothermally at 110°C with a series of different trap movements.

Figure 6(a) illustrates the regular GC elution condition without the cooling means being cooled. This represents a reasonably routine result which could be expected in such an analysis. Table 1 reports efficiencies obtained for each solute, along with peak asymmetries measured at 10% peak height (A_s) and widths at base (w_b). In Figure 6(b), the mechanism shown in Figure 5(a) is employed to trap each solute in turn, and then elute them from the cooled region by moving the cooling means immediately each whole chromatographic band has been focussed. Data reporting quality of the peaks as represented by the peak parameters, N, w_b and A_s are shown in Table 1.

Figure 6(c) is a separate analysis of the same mixture and process as Figure 6(a), but at a different carrier flow rate. Under these conditions Figure 6(d) illustrates the procedure outlined in Figure 5(b) but with the cooling commenced after C_{11} has passed the cooling means. Thus C_8-C_{11} were eluted in regular fashion but both C_{12} and C_{13} were collectively trapped and then eluted well after the usual retention time of C_{13}.

Example 2

C_{14} methyl ester was isothermally chromatographed under three different procedures: regular chromatography (no trapping); trap and elute with the ester remobilised just after being fully trapped by pushing the column through the 7 cm cooling means, and then the ester was trapped and the capillary moved in short steps (for example, 1 cm steps) through the cooling means with a delay of about 30 seconds

between each step.

Table 2 below illustrates the peak narrowing effects of the present invention when a cooling means is placed at the end of a column compared with conventional chromatographic techniques.

Table 2

	$C_{10}H_{22}$ w h	$C_{11}H_{24}$ w h	$C_{12}H_{26}$ w h	$C_{13}H_{28}$ w h
no cooling	2.04 63193	2.61 67063	3.8 57531	6.18 42683
cooling/move cooling	0.48 180351	0.38 270896	0.37 356408	0.44 366290

w=peak width/sec
h=peak height

From Table 2 it is apparent that the apparatus of the present invention results in narrower and taller peaks than chromatographs not having cooling means. The narrower peaks are a direct result of the more discrete, concentrated, bands of chemicals produced by moveable thermal modulation.

Table 3 below illustrates the peak narrowing affects of the present invention when a moveable cooling means is placed at the end of a column compared with conventional chromatographic techniques and chromatographic techniques using static cooling means.

Table 3

	C_{14} methyl ester	
	Peak width/sec	Peak height
1. no cooling	3.8	97323
2. cooling/turn off cooling	2.3	193874
3. cooling/move trap	0.47	798587

From the table it is apparent that the apparatus of the present invention results in narrower and taller peaks than chromatographs not having cooling means and chromatographs having cooling means which are not moveable along the column. The narrower peaks are a direct result of the more discrete, concentrated, bands of chemicals produced by moveable thermal modulation.

The heating of the column after the column has been cooled in trial 2 is slow, so the actual time that a peak appears in the detector is not readily predictable, and may occur 1 to 2 minutes after the cooling means is switched off. Using a moveable cooling means , the time that a peak will reach the detector is readily predicted.

The invention of the present application provides numerous advantages including the following:

- Less energy is required to immobilise the chemical sample as the cooling means is maintained at a constant temperature;
- The chemical sample may be cooled at any location along the conduit as the cooling means is moveable relative to the tube;
- Concentration of the chemical sample may be completed faster as time is not lost waiting for the

temperature of the cooling means to adjust;

- Any region of the conduit may be cooled as the cooling means is moveable relative to the conduit;
- Detector sensitivity may be increased by 5 to 10 times or more;
- Heat modulation may be rapid;
- Repeated heating and cooling events can be used;
- Narrower peaks are obtained which results in increased mass sensitivity in a detector and hence an ability to detect and measure lower levels of chemicals;
- Improved separation due to the narrowness of the bands;
- Large volume sampling may be possible;
- Detection modulation is possible by allowing concentrated pulses of sample to enter the detector;
- The time that a peak will reach a detector can be predicted;
- The cooling device does not require a heating element to be built within or as an integral part of the cooling means.

The described arrangement has been advanced by explanation and many modifications may be made without departing from the spirit and scope of the invention which includes every novel feature and novel combination of features hereindisclosed.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is understood that the invention includes all such variations and modifications which fall within the spirit and scope.

TABLE I

Comparison of chromatographic data reported for chromatograms in Figure 6(a) and 6(b). t_M ~ 2.1 min

solute	t_R, min	Area	Height	H/A ratio	Base width, s	N*	A_s#
FIG 6(a)							
C-8	2.52	23711	13701	0.578	3.2	35,720	1.25
C-9	2.91	76197	40560	0.532	3.5	39,820	1.21
C-10	3.63	136914	63193	0.461	4.1	45,150	1.15
C-11	5.00	186243	67063	0.360	5.2	53,250	1.01
C-12	7.57	232723	57531	0.247	7.6	57,150	0.76
C-13	12.39	280774	42683	0.152	12.4	57,500	0.55
FIG 6(b)							
C-8	2.65	15777	34046	2.17	0.89	510,700	1.01
C-9	3.16	48173	110195	2.27	0.83	834,900	1.02
C-10	3.98	91267	180351	1.96	0.95	1,011,000	1.02
C-11	5.38	108720	270896	2.50	0.77	2,812,000	1.00
C-12	7.87	139486	356408	2.56	0.75	6,342,000	0.99
C-13	12.67	173303	366290	2.13	0.88	11,940,000	1.02

* Efficiencies are based on theoretical plate values; values for Fig 6(b) are calculated directly for the given retention and width, so are 'apparent' values only, not actual.
# Asymmetry values (A_s) are determined as peak tail distance divided by peak front distance measured at 10% peak height

TABLE 4

Comparison of specific data for C-12 and C-13 in Figures 6c and 6d

	Fig 6c		Fig 6 d	
	C-12	C-13	C-12	C-13
Basewidth, s	10.0	14.0	1.3	1.4
t_R, min	9.23	15.08	17.30	17.36
A_s	0.93	0.88	1.01	0.96
Δt_R, s	289		3.6	
Rs	28.9		2.7	
N (C-12)	49,106		3,030*	
N, per metre	1,964		12,130	
H, mm	0.51		0.082	

* for C-12 in Fig 6d, the retention time used to calculate N is taken to be the time between moving the trap and recording the peak. This time is 17.9 sec. With a basewidth of 1.3 s, this gives 3,030 plates in the 25 cm length of column.

CLAIMS

1. An apparatus and/or device for the concentration of chemical components of a chemical sample comprising a conduit means and a cooling means, said conduit means having a receiving port for receiving the chemical sample and an outlet port for the expelling the chemical sample, said ports being in fluid communication with each other, said cooling means capable of cooling a portion of the conduit means and the chemical sample therein, said cooling means moveable relative to said conduit means such that at any one instant a portion of the conduit means and the chemical sample therein is cooled by the cooling means so that movement of the chemical sample therein is at least decreased.

2. An apparatus and/or device according to claim 1 wherein the apparatus and/or device is incorporated into or associated with a chromatographic column or spectroscopic, separation or detection apparatus.

3. An apparatus and/or device according to claim 2 wherein the chromatographic column is part of a supercritical fluid chromatograph, a gas liquid chromatograph, a gas solid chromatograph, a micro column liquid chromatograph or a high performance liquid chromatograph.

4. An apparatus and/or device according to any of the preceding claims wherein the conduit means forms part or all of the column.

5. An apparatus and/or device according to any of the preceding claims wherein the chromatographic column has two or more sections and the conduit forms part or all of each or both sections of the chromatographic column or the conduit means bridges the two sections.

6. An apparatus and/or device according to any of the preceding claims wherein the conduit is a tube which forms part of a column.

7. An apparatus and/or device according to claim 6 wherein the tube forms part of a liquid chromatography column, a capillary liquid chromatography column, a packed gas chromatography column, a capillary gas chromatography column or a supercritical fluid column.

8. An apparatus and/or device according to any of the preceding claims wherein the cooling means is between 0.1 mm and 500 mm in length.

9. An apparatus and/or device according to any of the preceding claims wherein the cooling means comprises a hollow sleeve having one or more entry ports in fluid communication with the hollow and one or more exit ports in fluid communication with the hollow and wherein cool coolant gas flows through the entry ports into the hollow and out the exit ports.

10. An apparatus and/or device according to any of the preceding claims wherein the cooling means comprises a slotted tube wherein part of the conduit is brought into the cooling means by insertion into the cooled slot.

11. An apparatus and/or device according to any of the preceding claims wherein the cooling means may be moved relative to the conduit in the direction of flow of the chemical sample and alternatively, against the direction of flow.

12. An apparatus and/or device according to any of the preceding claims wherein the cooling means is moved relative to the conduit at a rate of greater than 5 times

per second.

13. An apparatus and/or device according to any of the preceding claims wherein the cooling means is moved relative to the conduit at a rate of between 1 cm per second and 20 cms per second.

14. An apparatus and/or device according to any of the preceding claims wherein the movement of the cooling device is pre-programmed and controlled by computer.

15. An apparatus and/or device according to any of the preceding claims wherein the cooling means can cool the chemical sample to a temperature between -20 °C and 100 °C.

16. An apparatus and/or device according to any of the preceding claims wherein at least part of the portion of the conduit not subjected to the cooling means is subjected to a heating means.

17. An apparatus and/or device according to any of the preceding claims wherein the conduit comprises a first section, a connecting section and a second section wherein the cooling means is moveable along the connecting section.

18. An apparatus and/or device according to claim 17 wherein the connecting section is a concentrating section and the first and second sections are separating sections which each comprise a housing which has a variable temperature of between ambient and 300 °C.

19. An apparatus and/or device according to any of the preceding claims which comprises a second cooling means.

20. An apparatus and/or device according to claim 18

which comprises a second concentrating section on which is located a second cooling means.

21. An apparatus and/or device according to any of the preceding claims wherein the conduit is branched and the cooling means is positioned in an area before the branch.

22. A method of concentrating chemicals using the apparatus and/or device of any of the preceding claims, the method comprising the steps of;

a) inserting a chemical sample into a conduit and allowing the chemical sample to travel through the conduit,
b) cooling a first portion of the conduit to a predetermined temperature and maintaining the predetermined temperature using the cooling means,
c) accumulating within the first portion of the conduit for a predetermined period of time a portion of the chemical sample, thus forming a first concentrated band,
d) moving the cooling means to a second portion of the conduit and allowing the first portion of the conduit to warm so as to release the first concentrated band of the chemical sample within the first portion of the conduit, and
e) repeating steps c) to d) as required.

23. A method according to claim 22 wherein the conduit comprises a carrier fluid.

24. An apparatus and/or device substantially as herein described with reference to the drawings.

25. A method substantially as herein described with reference to the drawings.

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AMENDED CLAIMS

[received by the International Bureau on 11 February 1998 (11.02.98); original claim 1 amended; remaining claims unchanged (2 pages)]

1. An apparatus and/or device for the concentration of chemical components of a chemical sample comprising a conduit means and a cooling means, said conduit means having a receiving port for receiving the chemical sample and an outlet port for the expelling the chemical sample, said ports being in fluid communication with each other, said cooling means capable of cooling a portion of the conduit means and the chemical sample therein, said cooling means moveable relative to said conduit means such that at any one instant a portion of the conduit means and the chemical sample therein is cooled by the cooling means so that movement of the chemical sample therein is at least decreased, and wherein the apparatus does not include a partitioned heating chamber or a movable baffle plate for controlling the temperature of the conduit means.

2. An apparatus and/or device according to claim 1 wherein the apparatus and/or device is incorporated into or associated with a chromatographic column or spectroscopic, separation or detection apparatus.

3. An apparatus and/or device according to claim 2 wherein the chromatographic column is part of a supercritical fluid chromatograph, a gas liquid chromatograph, a gas solid chromatograph, a micro column liquid chromatograph or a high performance liquid chromatograph.

4. An apparatus and/or device according to any of the preceding claims wherein the conduit means forms part or all of the column.

5. An apparatus and/or device according to any of the preceding claims wherein the chromatographic column has two or more sections and the conduit forms part or all of

each or both sections of the chromatographic column or the conduit means bridges the two sections.

Statement Under Article 19

It is noted that 3 citations have been referred to in the International Search Report of which one is classified in category X and the other two are classified in category A.

In response the claims have been revised by amending the wording of claim 1.

It is submitted that amendment of claim 1 has overcome the category X citation, SU-1343349 (Kuib University). It is submitted that the invention defined in the amended claim is clearly distinguished from this ciatation for the following reasons.

The invention described in the citation is a temperature programmed gas chromatograph which comprises a chromatographic column placed in a thermostated, heated chamber partitioned into two sub-chambers by a moveable baffle plate. The baffle plate may be moved for example, by a programmed worm-gear drive. The baffle plate comprises a spiral-type cooler, through which the chromatographic column passes.

Conversely the invention of the present application does not utilise a heating chamber partitioned by a movable baffle plate. The invention of the present application and the invention described in the cited art therefore operate in quite different manners, using quite different heating/cooling.

Figure 1

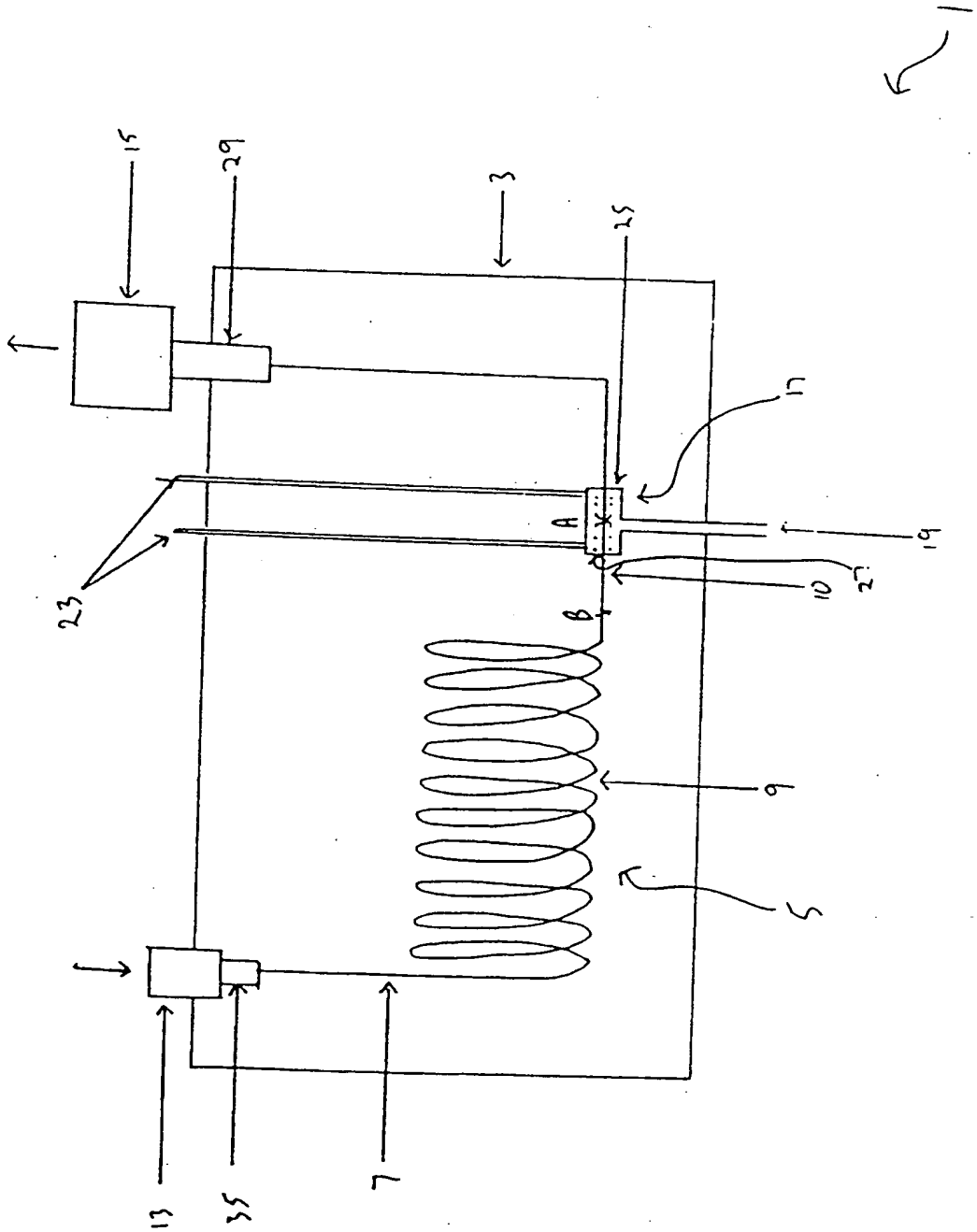


Figure 2

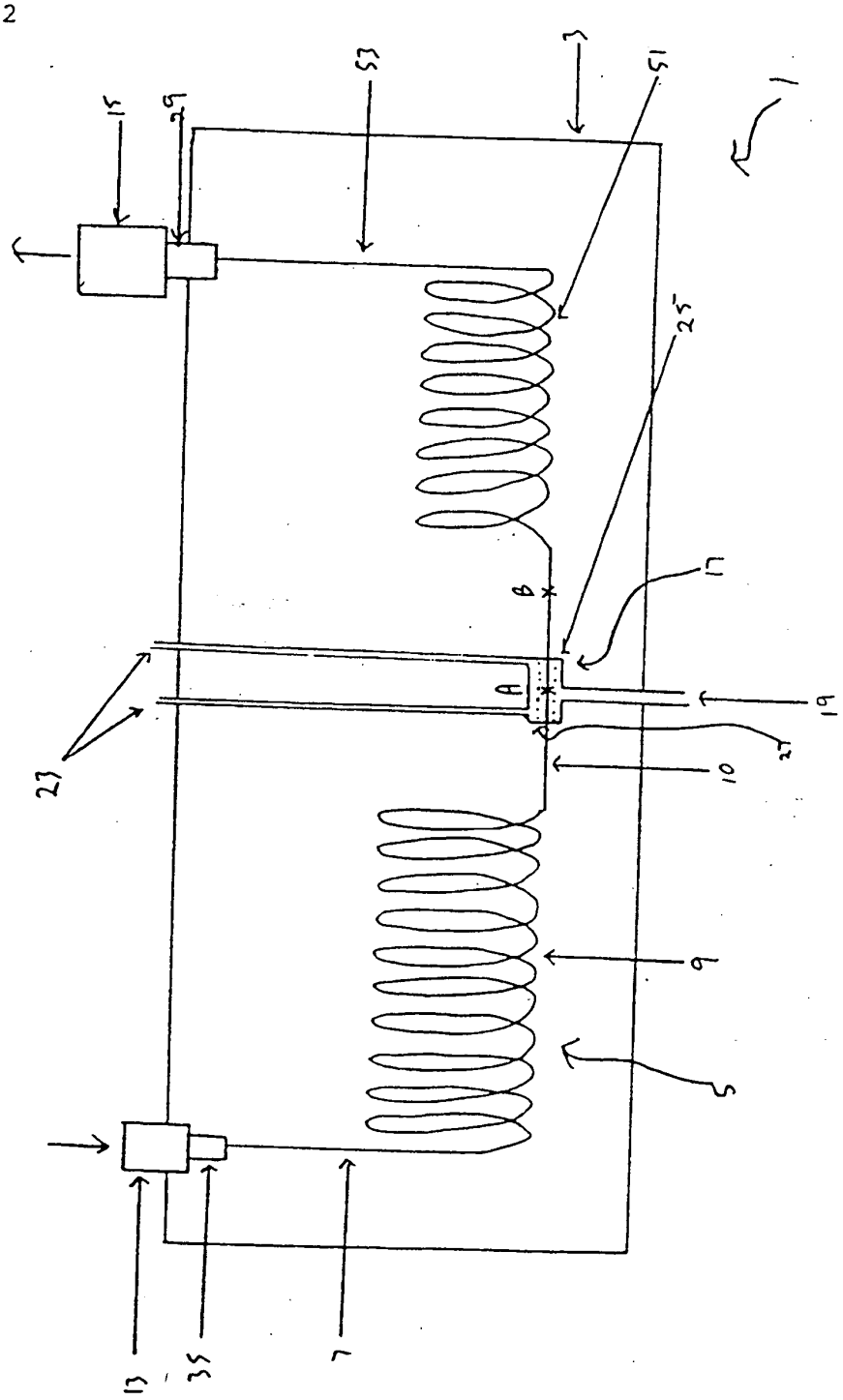


Figure 3

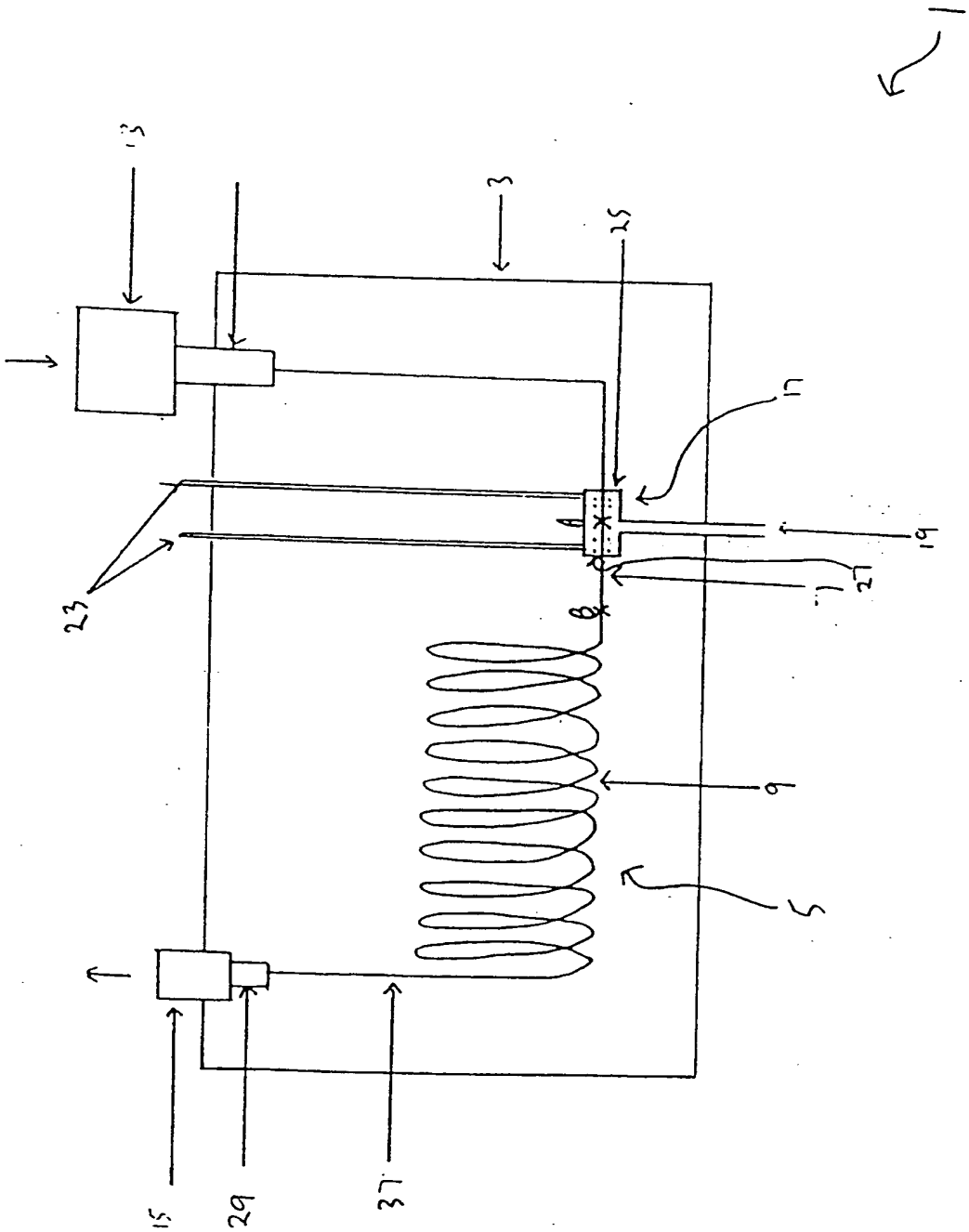
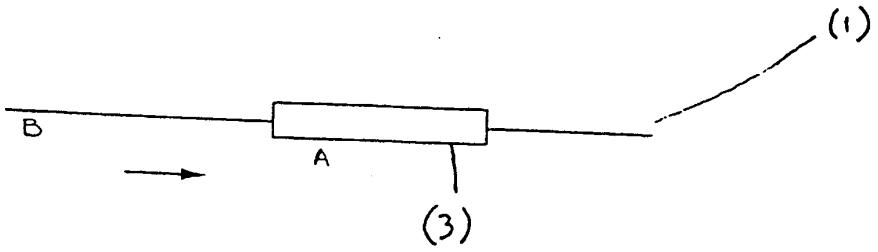


Figure 4

a



b

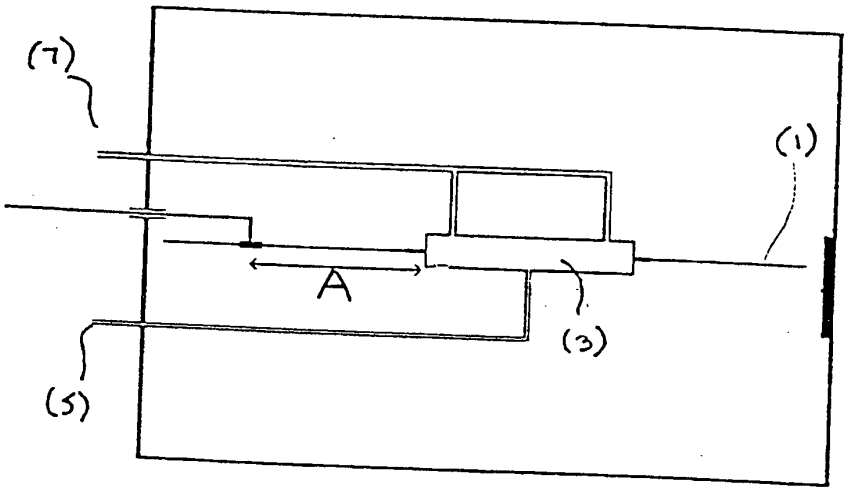


Figure 5

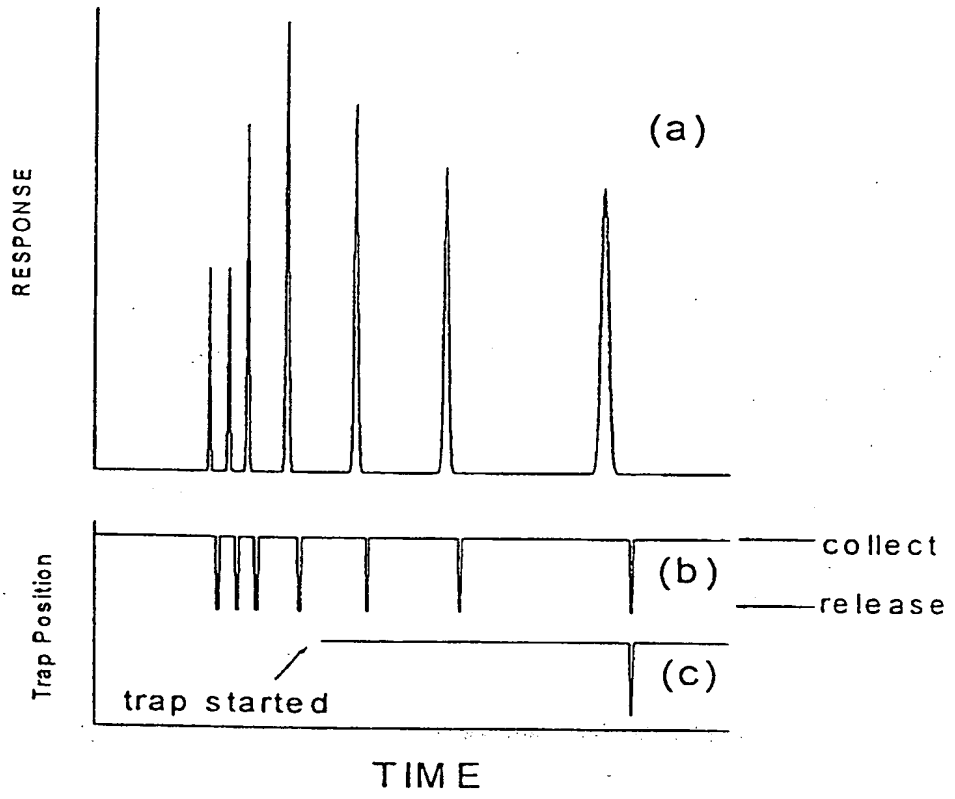


Figure 6a

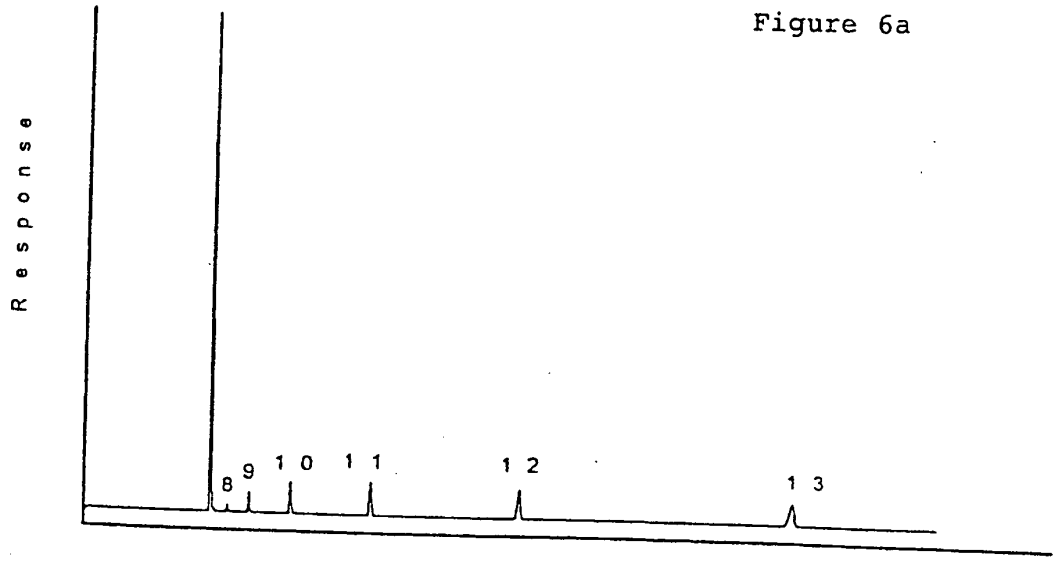


Figure 6b

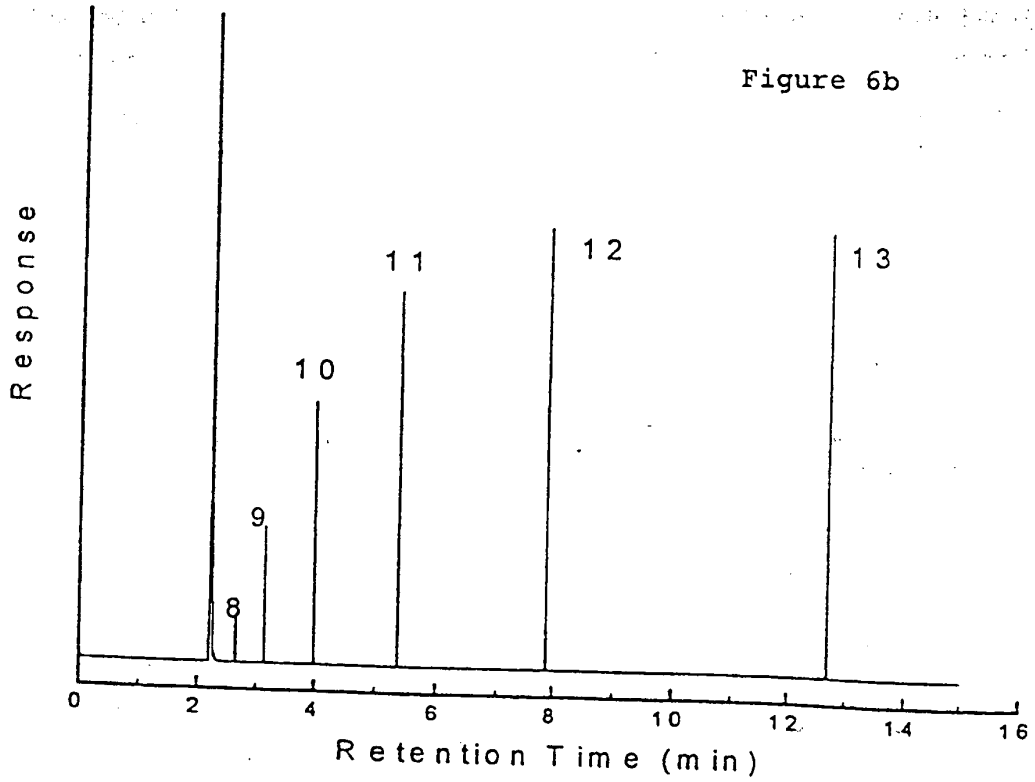


Figure 6c

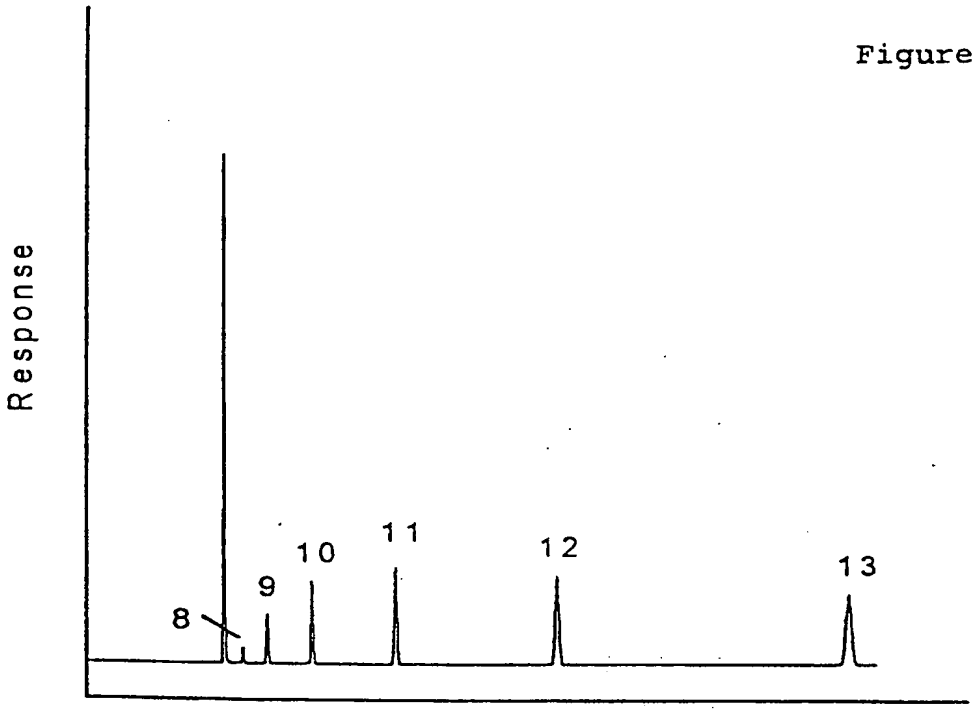


Figure 6d

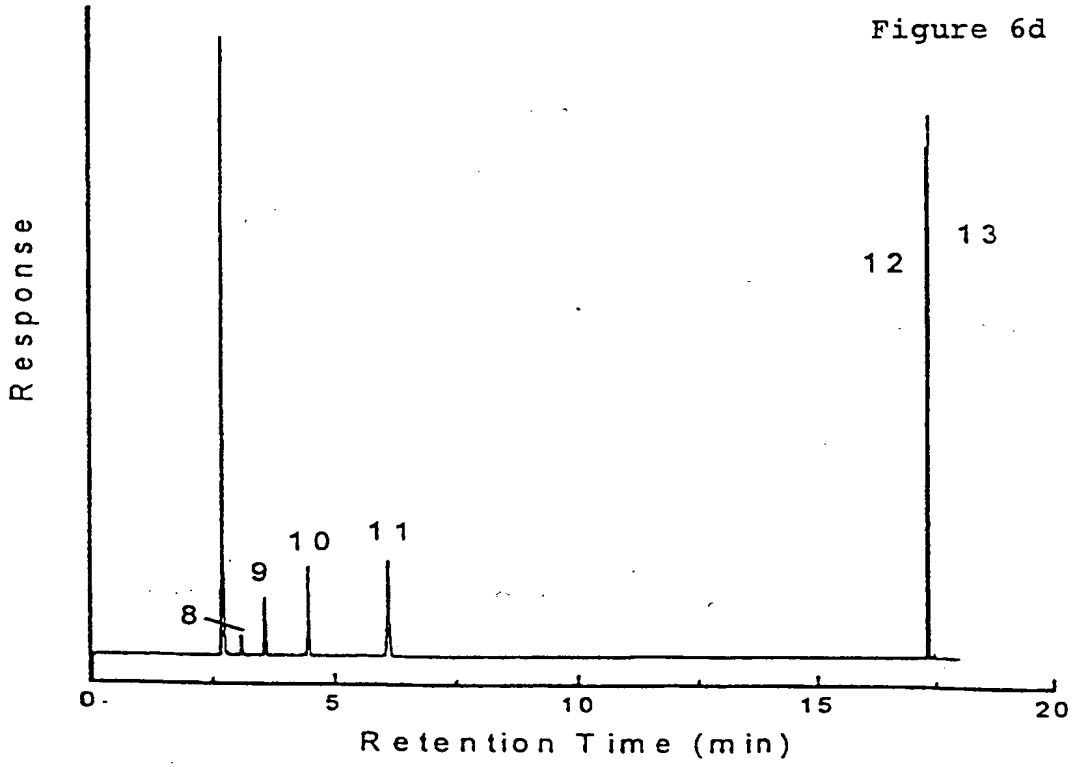


Figure 6e

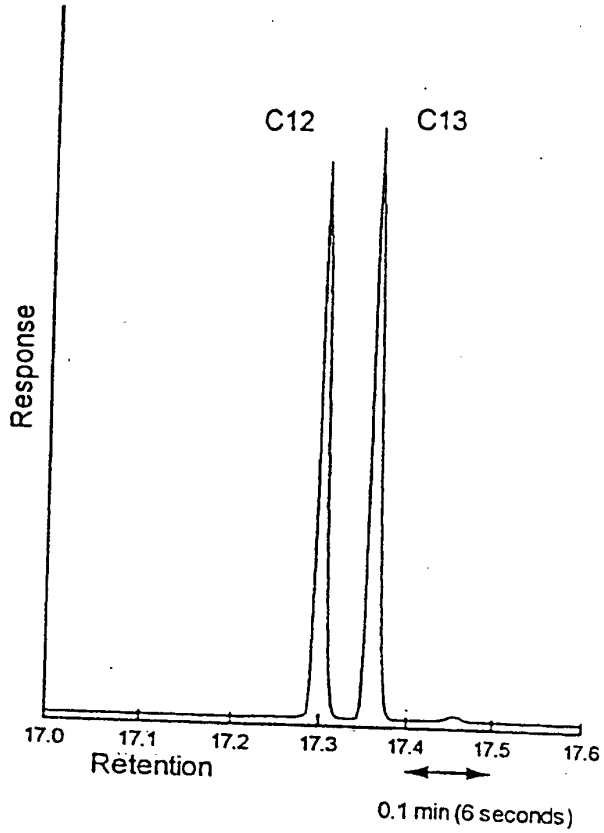
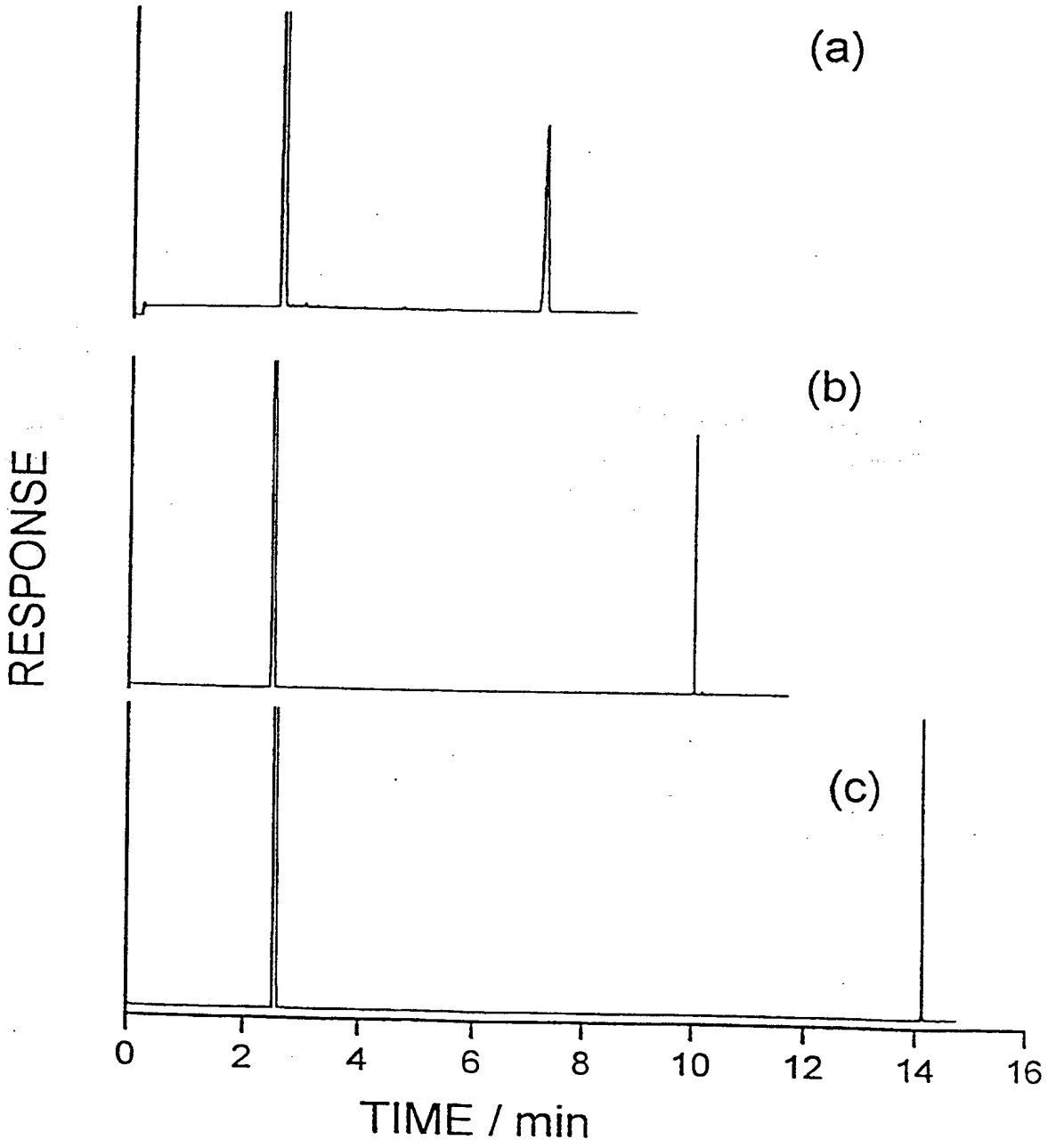

C12
C13
Response
17.0
17.1
17.2
17.3
17.4
17.5
17.6
Retention
0.1 min (6 seconds)

Figure 7



INTERNATIONAL SEARCH REPORT

International Application No.
PCT/97/00764

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl[6]: G01N 30/06, 30/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC[6] G01N 1/28, 1/40, 1/44; 30/06, 30/08, 30/10, 30/12, 30/14, 30/30, 30/34, 30/84

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent WPAT On line Abstract Accession No. 88-131605 SU 1343349 A (KUIB UNIVERSITY) 07 October 1987 abstract	1-23
A	WO 96/00388 A2 (UNIVERSITE DE MONTREAL) 04 January 1996 abstract and figures	1-23
A	Derwent WPAT Online Abstract Accession No: 81-60473D BE 888 304 (CHOCOLATERIE CALLEB) 31 July 1981 abstract	1-23

☐ Further documents are listed in the continuation of Box C

☒ See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 December 1997	12 DEC 1997
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929	Authorized officer **GREG POWELL** Telephone No.: (02) 6283 2308

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INTERNATIONAL SEARCH REPORT

International Application No.
PCT/97/00764

Box 1 Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 24, 25
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
the scope of the claims is indeterminate because they refer to the description. (Rule 6.3)

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.
PCT/97/00764

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member	
SU	NONE		
WO	96/00388	AU	27819/95
BE	NONE		

END OF ANNEX